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RESEARCH & DEVELOPMENT OF A HIGH CAPACITY NONAQUEOUS SECONDARY BATTERY

FIRST QUARTERLY REPORT

CONTRACT No. NAS 3-6017

prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA
Lewis Research Center
Space Power System Division
21000 Brookpark Road
Cleveland, Ohio

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ABSTRACT

Our basic investigations with solid electrodes were directed towards a more efficient process for screening electrolyte systems with respect to the electrokinetics of electrode processes.

A discussion of the general theory pertaining to electrochemical measurements under the conditions of dilute solutions and in the total absence of supporting electrolyte is presented. This discussion introduces the concept of effective d_L , the distance between the tip of a hypothetical Luggin capillary and the surface of the electrode.

Measurements of d_L in aqueous, unsupported solutions of AgClO_4 and AgNO_3 were carried out, giving a value of 0.157 ± 0.007 cm. for the lollipop electrode structures used. Variations in the concentration of silver ion gave a log plot slope of 0.12 V and additions of supporting electrolyte reduced the value of $iT^{1/2}/C_{\text{Ag}^+}$ by one half as predicted by theory. A wide variety of other salt systems were similarly examined giving consistent values of effective d_L and making it clear that meaningful electrochemical measurements may be made in the absence of supporting electrolyte on solid electrodes.

Attention was then turned to similar experiments in unsupported non-aqueous solutions. A study of AgClO_4 in propylene carbonate gave an effective d_L of 0.150 cm. and the addition of LiClO_4 supporting electrolyte reduced $iT^{1/2}/C_{\text{Ag}^+}$ by one half. However, the slope of the log plot for the unsupported solution gave the unexpectedly high value of 0.20V. rather than 0.12V. Experiments with unsupported LiClO_4 in propylene carbonate revealed the following facts:

- a. Satisfactory steady state E-i curves cannot be obtained.
- b. At potentials positive to the lithium deposition potential background reduction does occur.

c. When the E-i curves for lithium reduction are corrected for iR drop using an effective d_L of 0.157 cm., the efficiency for lithium deposition is a constant 80% up to about -0.2 to -0.3 V versus the open circuit potential of a lithium electrode in the same solution.

d. At potentials more negative than about -0.3 V. versus the lithium deposition potential, the amount of current consumed in forming metallic lithium decreases and a black film of Li_2O or $LiOH$ is formed as a result of side reactions which consume the remainder of the current. Solutions of $LiCl$, CsF , KI , and $KCNS$ in propylene carbonate were examined and the results in each case are discussed and compared.

In order to prepare for practical cell studies, the chronopotentiometric behavior of flat and porous electrodes was studied in aqueous copper sulfate solution. A plot of iT versus $1/i$ was linear for the flat electrode and curved for the porous electrode. Such curves, reflecting the changes in internal surface area and concentration, can be used to characterize and study porous electrode configurations and to optimize their performance. Such curves also show that the amount of electro-active material that can be loaded on a porous electrode is higher than for a flat electrode with the difference depending on current density.

Practical cells were constructed comprising a lithium anode and a copper chloride cathode, and employing an electrolyte of lithium chloride dissolved in dimethylformamide. On charge lithium is deposited from solution onto an aluminum substrate, and the copper electrode is anodically oxidized to higher valent copper chloride species. The behavior of the lithium electrode is surprisingly good and anodic efficiencies of 90-95% were obtained. The potential of the lithium electrode was investigated in solutions of $LiCl$ in DMF over four decades of concentration. The variation in potential with respect to concentration was exactly that predicted by the Nernst equation for a one-electron redox system; however, the potential of the lithium electrode is about .5 V more positive than in propylene carbonate or butyrolactone.

Self-discharge of the cell is large and it was determined that short term self-discharge does not result from reaction of the lithium metal with solvent. A concerted study of the self-discharge mechanism was carried out and it appears that it results from the high solubility of the copper species produced on charge. This was established by spectrophotometric experiments which show that copper (II) is quite soluble in the LiCl-DMF electrolytes and by examination of a used cell which revealed that the separator becomes yellowed through impregnation by soluble copper salts, and the aluminum substrate shows corrosion attack with formation of copper metal on the substrate. The measured solubilities of CuCl and CuCl₂ are both greater than $5 \times 10^{-4} \text{ M l}^{-1}$ which is sufficient to account for the observed self-discharge of the cell. Efforts to reduce the solubility of copper chlorides in DMF by the use of the common ion effect, mixed solvents, and complexing anions were not effective.

Because of the solubility induced self-discharge problem found in the chloride containing cells, a study of an all-fluoride containing cell system was initiated. Preliminary results with cells composed of lithium anodes, lithium fluoride-boron trifluoride - γ -butyrolactone electrolytes, and copper cathodes were encouraging. Lithium fluoride is very soluble in butyrolactone in the presence of boron trifluoride yielding solutions with a conductivity about equal to that expected from the metathetical formation of ionized LiBF₄ from which lithium can be reversibly deposited. However, such cells have extremely large background currents which apparently arise through the reduction of impurities resulting from solvent decomposition which occurs during the mixing of boron trifluoride and butyrolactone. Consequently better methods of electrolyte preparation are being actively pursued.

I. INTRODUCTION

The objective of our program is the development of a secondary cell capable of operating for 100 cycles at 25% depth of discharge at 10 mA cm⁻² apparent electrode area at 20°C. The initial phase of our effort has been to determine the basic problems and fundamental limitations inherent in various non-aqueous systems so that a systematic and effective screening program can be developed. The following conclusions have been reached:

1. The solubility of cathodic salts is too great. Solubilities must be reduced to less than about 10⁻⁴M and a useful screening program must indicate those electrolytes in which this limit is not exceeded.
2. The reversibility of the lithium electrode is not satisfactorily efficient. This results from the mechanism by which lithium metal is deposited and is a function of both the solvent and the solute. A useful screening program must be critically sensitive to this phenomenon.
3. The preparation and purification of electrolytes -- solvent and solute -- is of extreme importance. A useful screening program must take cognizance of the fact that as yet adequate means for the investigation of solvent impurities and the catalytic decomposition of electrolyte do not exist.
4. Electrode fabrication is dependent on the particular nature of the electrode reaction. A useful screening program must not be one in which desirable electrochemical properties may be obscured by the particular type of electrode design employed.
5. Conductivity is also important. However, one of the fundamental limitations to the operation of primary or secondary batteries lies not in IR losses in that portion of the electrolyte between the two electrodes but in the rate with which electroactive participants can be supplied to the electroactive sites.

With these considerations in mind a detailed screening program has been

developed which is described in the final section of this report. In making useful electrochemical measurements as part of a screening program, we have been most recently concerned with the general question of the utility and validity of electrochemical measurements in the absence of supporting electrolyte and in dilute solution. In section II the results of this study are presented in some detail. We further describe the behavior of the particular type of electrode system we have employed in our work. We are encouraged by the simplicity with which useful information can be obtained and suggest the inclusion of such experiments in any program in which non-aqueous electrolyte systems are characterized in order that data relevant to battery operation may, finally, be acquired.

In Section III the results of studies performed on prototype cells are presented. It is from such studies that the conclusions voiced above have been drawn.

II. Electrochemical Studies in the Absence of Supporting Electrolyte

A. Introduction

In our investigations of electrode reactions in such non-aqueous solvents as propylene carbonate, butyrolactone, and dimethylformamide we have been constrained to work in the absence of supporting electrolyte because few salts are both sufficiently innocuous with respect to their participation in electrode reactions and sufficiently soluble to serve as supporting electrolytes in these solvents. Furthermore, we have worked exclusively with a particular type of electrode system, which, though superbly adapted for experimentation with solid electrodes, results in the inclusion of certain geometric parameters in the electrochemical measurements, namely the diffusion layer thickness and an effective d_L , later described.

In the past we have concentrated our research on those relatively few systems most amenable to study by virtue of the solute being soluble to the extent of at least 0.1 M l^{-1} . This approach must now be expanded into an examination of more dilute solutions and an evaluation of electrokinetic parameters. During this quarter we have devoted considerable time to an examination of the general area of electrochemical measurements in the total absence of supporting electrolyte and the limits within which meaningful electrochemical data, particularly electrokinetic parameters, may be obtained in dilute solutions in the total absence of supporting electrolyte.

In this section of the report we discuss the general theory pertaining to electrochemical measurements under the conditions described above, the results of our work in dilute aqueous solution, and further investigations into the behavior of various solutes in propylene carbonate.

B. Theory

When current is applied to a working electrode, W.E., the measured

potential difference, E_M , between the W.E. and the reference electrode, R.E., is:

$$E_M = E_O + E_K + E_C + E_{R\text{-diff}} + E_{R\text{-soln}} \quad (1)$$

E_O = the open circuit potential of the W.E. vs. the R.E.

E_K = kinetic overvoltage, which, in this discussion, includes activation (transfer) overvoltage, crystallization overvoltage, and parameters reflecting the nature of the electrode surface.

$E_{R\text{-soln}}$ = the resistance polarization across the solution between the boundary of the diffusion layer and that point at which the reference electrode effectively probes a fraction of the total iR drop between the working electrode and the counter electrode. It should be noted that the thickness of the diffusion layer is only a few percent of the total distance between the surface of the working electrode and the point of effective probing by the reference electrode, and it is thus inconsequential whether one considers the total distance across which iR drop is probed to include the diffusion layer thickness or not.

E_C = concentration overvoltage, resulting from the fact that during electrolysis the concentration of electroactive material at the electrode surface differs from that in the bulk of solution.

$E_{R\text{-diff}}$ = the potential difference existing across the diffusion layer, resulting from the fact that during electrolysis the concentration of ionic species at the electrode surface differs from that in the bulk of solution. It is sometimes convenient to consider this potential difference as a type of iR drop across the diffusion layer. It is because of the existence of this potential difference that ions move by electrical migration as well as by diffusion.

The primary objective of electrokinetic studies is the development of a mechanistic description of a given electrode reaction. This entails a study of the relationship between E_O , E_K , E_C , the current density, and the concentration of the various participants in the reaction. One must either eliminate or accurately correct for $E_{R\text{-diff}}$ and $E_{R\text{-soln}}$. These two terms are normally reduced to negligible values by the addition of excess supporting electrolyte and by the use of a closely positioned Luggin capillary through which electrical contact between the R.E. and the W.E. is provided. A further important function of supporting electrolyte is the maintenance of constant ionic strength and one may thus assume constant activity coefficients for the electroactive species.

For brevity we consider but one type of electrode reaction: $M^{+n} + n e^- = M^O$ -- the discharge of a metal ion to the metal on a substrate of the same metal. We consider a reversible reaction wherein E_K in equation 1 vanishes, and a totally irreversible reaction. We consider two common techniques of electrochemical investigation, one in which constant current is passed in stirred solution, and in which the steady state value of the potential is measured. The full series of experiments comprises measurements over a wide range of currents. (Note: Identical results are ideally realized if the potential is maintained constant and the steady state current measured.) A plot of current versus potential is a polarization curve, here called simply an i-E curve. The second technique of investigation is one in which constant current is passed in quiet solution, and the variation in potential with time recorded. The plot of potential versus time (normally automatically recorded) is a chronopotentiogram or charging curve, here called simply an E-t curve.

The following equations describe i-E and E-t curves:

Reversible electrode reaction: i-E curve

$$E_M = E_O + (k_C + k_D) \log \left(1 - \frac{i}{i_D} \right) - i R_{\text{spec}} d_L \quad (2)$$

Reversible electrode reaction: E-t curve

$$E_M = E_O + (k_C + k_D) \log \left(1 - \frac{t^{1/2}}{T^{1/2}} \right) - iR_{\text{spec}} d_L \quad (3)$$

Totally irreversible electrode reaction: i-E curve

$$E_M = E_O - A - B \log i + (B + k_D) \log \left(1 - \frac{i}{i_D} \right) - iR_{\text{spec}} d_L \quad (4)$$

Totally irreversible electrode reaction: E-t curve

$$E_M = E_O - A - B \log i + (B + k_D) \log \left(1 - \frac{t^{1/2}}{T^{1/2}} \right) - iR_{\text{spec}} d_L \quad (5)$$

The terms appearing in equations 2-5 are defined:

k_C = a constant which, multiplied by the logarithm term gives E_C .
 k_C is the Nernst equation constant, RT/nF , and with Briggsian logarithms is, at room temperature, 0.059/n.

k_D = a constant which, multiplied by the logarithm term gives $E_{R\text{-diff}}$. k_D is identical in form to k_C , however the term "n" is the charge of the counter ion, not the reduceable ion. Thus, for example, in the reduction of CuCl_2 the n to be used in k_C is 2, that to be used in k_D is 1. Equations 2-5 are so written that absolute values for n are to be used.

i = current density

i_D = the limiting current density

R_{spec} = the specific resistance

d_L = the distance between the tip of the Luggin capillary and the boundary of the diffusion layer. Ideally, the last term in equations 2-5 represents the total iR drop across that cylinder of solution between a Luggin capillary of area A_L and a parallel

area A_L on an electrode of total area A_T . When the total current is i_T the iR drop actually measured is that fraction of the total current flowing through this cylinder of solution multiplied by the resistance of the cylinder, thus:

$$iR = \frac{i_T \cdot a_L}{a_T} \times \frac{R_{\text{spec}} \cdot d_L}{a_L}$$

and the area of the capillary tip cancels out. Of course $i_T/a_T = i$, the current density.

t = the time elapsed after the initiation of current flow.

T = the transition time

A = the Tafel constant

B = the Tafel slope

Equations 2 and 3 and equations 4 and 5 are identical except for the logarithm term. It will be convenient to make the following substitution hereafter:

$$\frac{i}{i_D} = x_i \cdot \frac{t^{1/2}}{T^{1/2}} = x_t$$

For a reversible system a plot of E_M versus x_i should be identical to one of E_M versus x_t after corrections have been made for the last term in equation 2 and 3.

The magnitude of the quantities appearing in equations 2-5 have been found to be such that for a typical, irreversible, one electron reduction the i - E curve described by equation 4 would be approximately:

$$E_M = E_O - A - .12 \log i + .18 \log (1-x_i) - (1.0) i$$

in which E will be in volts if the current is expressed in mA cm^{-2} . The coefficient in the last term is the product of d_L and a typical specific resistance. We assume a Tafel slope of .12 (an exchange coefficient of .5). At moderate currents where i is from 10% to 90% of the limiting current, the logarithm term varies

such that the apparent slope of E_M versus i is linear. This is not pure ohmic polarization but results from the particular nature of the logarithmic expression in this current range. At sufficiently low currents the last two terms vanish but not the $\log i$ term. We have not been able to make measurements at such low currents because of extensive background reduction. We must work in a region of current density where the appropriate corrections must be made.

C. Experimental

1. Procedure. In our work contact between the W.E. and the R.E. is not made via a Luggin capillary. The electrode system consists of a cylinder about 1 1/2" in diameter and 3/4 to 1" deep. The cylinder is filled with epoxy and in one face are imbedded small discs sliced from rods of high purity metals, each disc being 0.50 cm in diameter (area = 0.196 cm²). One silver disc is positioned approximately in the center of one face of the cylinder, five or six other discs are positioned concentrically about the center disc. The center disc serves as the reference electrode either without treatment or following electrolytic pre-treatment (e.g. in halide media the silver may be anodized to the silver halide and the silver disc with the electrodeposited halide film serves as a good R.E. In media containing reduceable metal ions (Li⁺, Cu⁺⁺, Pb⁺⁺) the metal may be deposited on the silver electrode and the resultant surface functions as a good R.E.) The concentric discs serve as working electrodes. The entire electrode is immersed in 200 ml. of solution contained in one compartment of an H-cell; the other compartment containing the same solution has immersed in it a platinum wire which serves as the counter electrode. Significant diffusion of reaction products through the sintered glass disc separating the two compartments does not occur. Stirring is provided by a variable speed magnetic stirrer of conventional design (e.g. Fisher Flexa-Mix, catalogue No. 14-511-1, or Sargent Variable Speed Magnetic Stirrer, catalogue No. S-76490).

In our electrical circuitry the working electrode is grounded and

the reference electrode potential is measured either by an electrometer feeding a Varian G-14 recorder or by an oscilloscope. Current is supplied by either an electronic constant current supply or by a Wenking potentiostat.

2. Results. We were first concerned with whether an effective and constant d_L term exists for the particular type of electrode configuration employed so that, once known, corrections for iR drop can be easily made as shown in equations 2-5. Secondly, we were concerned with the effective mass transfer parameters in the absence of supporting electrolyte and in investigating the relative importance of the k_C , k_D , and B terms in equations 2-5. Finally, we are interested in applying these results to a re-examination of earlier data obtained in non-aqueous solutions.

a. Electrochemical measurements in aqueous solution in the total absence of supporting electrolyte.

(1) Measurement of effective d_L in aqueous $AgClO_4$.

Solutions of $AgClO_4$ were initially examined since the discharge of the silver ion is reversible and described by equations 2 and 3. Further the salt is comprised of two monovalent ions and is thus similar to most of the salts considered for use in non-aqueous electrolytes. In addition the center silver disc served as the reference electrode without further treatment and the potential at which faradaic processes commence should be the open circuit potential -- there should be no double layer charging before the onset of discharge. A solution only 0.0021 M in $AgClO_4$ was used.

Experiment 1

Equation 3 was applied. $E_O = 0$ and at $t = 0$ the measured potential should be equal to $iR_{spec} d_L$. Obtaining a meaningful potential at $t = 0$ is not quite so obvious, however. The response time of the recorder is about 0.5 seconds full scale and this will be reflected in the apparent initial potential as will the

amount of damping. Furthermore, surface effects may cause the initial potential to deviate from the ideal value. Three methods for obtaining the potential at $t = 0$ were used: (1) visual inspection in which the $E-t$ curve was extrapolated by eye to $t = 0$; (2) plots of $\log(1-x_t)$ were made and extrapolated to $x_t = 0$; (3) In an essentially equivalent procedure the potential was measured one second after the initiation of electrolysis and corrected for the log term using, for $k_C + k_D$, the value of 0.12 (See next section). The results are shown in Table 1 below and are given in some detail to show the general magnitude and accuracy of the quantities involved in this type of study.

TABLE 1
Measurement of d_L

Current on 0.196cm ² electrode <u>mA</u>	Transition time <u>sec</u>	E_M by method 1 <u>V</u>	E_M by method 2 <u>V</u>	E_M by method 3 <u>V</u>	Correction for $.12\log(1-x_t)$ <u>V</u>	d_L <u>cm</u>
0.050	19.6	.180	.183	.189	-0.014=.176	.183
0.056	15.8	.200	.195	.210	-0.015=.195	.181
0.070	10.0	.245	.231	.255	-0.020=.235	.174
0.085	6.9	.300	.276	.310	-0.025=.285	.174
0.100	4.9	.350	.334	.370	-0.031=.339	.176

Each of the above results were obtained on a freshly polished electrode. The effects of the surface were seen when an electrode was anodically etched (50 mC cm^{-2}) or on which silver was deposited cathodically (50 mC cm^{-2}). In both cases the initial potential at a current of 0.050 mA decreased to 0.160 V ($d_L = 0.163 \text{ cm}$). Because of evident surface effects we do not have much confidence in the results shown in Table 1.

Experiment 2

Again equation 3 was applied. In this case, however, the initial potential was measured using an oscilloscope set at 0.02 seconds per full sweep. The voltage scales were so adjusted that the visual error in potential reading of the

photographically recorded oscillographs was less than 5%. The results are shown in Table 2 below.

TABLE 2
Measurements of d_L

Current on 0.196 cm^2 electrode	Initial Potential	d_L
<u>mA</u>	<u>V</u>	<u>cm</u>
0.030	0.09	0.156
0.060	0.17	0.147
0.090	0.26	0.150
0.150	0.45	0.156
0.180	0.54	0.156
		Average = 0.153
		± 0.008

Similar experiments were performed in which the electrode was polarized anodically (oxidation of Ag^0 to Ag^+) and the initial potential measured oscillographically. The results are shown in Table 3 below.

TABLE 3
Measurement of d_L

Current on 0.196 cm^2 electrode	Initial Potential	d_L
<u>mA</u>	<u>V</u>	<u>cm</u>
0.030	0.09	0.156
0.060	0.18	0.156
0.090	0.27	0.156
0.120	0.37	0.160
0.150	0.46	0.159
		Average = 0.157
		± 0.003

Experiment 3

Equation 2 was applied. The limiting current was measured and found to be about 0.225 mA on the 0.196 cm^2 electrode. In the conditions of turbulent flow which prevail in our systems the limiting current oscillates about the average at about a cycle per second but the average value is quite clearly observed when the current is recorded for at least a minute and we estimate an error of no more than 5% for the limiting current. The measured potential was that set on the potentiostat and this was corrected for the log term using the value of 0.12 for $k_C + k_D$ found chronopotentiometrically (see next section). The results are shown in Table 4 below:

TABLE 4
Measurement of d_L

Current on 0.196 cm^2 electrode	E_M	$.12 \log(1 - \frac{i}{.225})$	$E_{\text{corrected}}$	d_L
<u>mA</u>	<u>V</u>	<u>V</u>	<u>V</u>	<u>cm</u>
0.017	0.055	0.005	0.055	0.153
0.032	0.005	0.007	0.098	0.159
0.047	0.150	0.012	0.143	0.158
0.062	0.205	0.014	0.191	0.160
0.078	0.255	0.020	0.235	0.156
0.092	0.305	0.023	0.282	0.159
				Average = 0.157 ± 0.004

Experiment 4

Equation 2 was applied. Constant current anodizations were performed in stirred solution. In this case silver ions are being injected into the solution and since there is no depletion of ions in the region next to the electrode limiting currents are not obtained in stirred solution nor are transition times obtained in quiet solution. In this case the logarithmic term of equation 2 has the form $(k_C + k_D) \log(1 + \frac{i}{i_D})$. The results are shown in Table 5.

TABLE 5
Measurement of d_L

Current on 0.196 cm ² electrode mA	E_M V	$.12 \log (1 + \frac{i}{.225})$ V	E corrected V	d_L cm
0.030	0.113	0.006	0.107	0.154
0.060	0.218	0.012	0.206	0.163
0.090	0.323	0.018	0.305	0.155
0.120	0.418	0.022	0.396	0.164
0.150	0.528	0.026	0.492	<u>0.164</u>
				Average = 0.162 ± 0.008

We had previously observed that the results did not vary from one electrode to another as much as did the estimated error in measurements. The placement of the electrode assembly with respect to the counter electrode did not significantly affect the results. We estimate an effective d_L of 0.157 ± 0.007 cm (5% variation).

(2) Measurement of effective d_L in aqueous AgNO_3

Similar studies were conducted in 0.002 M AgNO_3 . The specific resistance was measured to be 3831 ohm-cm. The value of $iT^{1/2}$ at transition times of from 4 to 20 seconds was 0.264 ± 0.004 mA sec^{1/2} on the 0.196 cm² electrodes. Effective d_L 's were measured in the same fashion as in the preceding experiments. The results are shown in Table 6 below.

TABLE 6
Measurement of d_L

<u>Method</u>	<u>Range of measurement</u>	<u>d_L</u>
Potentials obtained on cathodic chronopotentiometry at $t = 0$ obtained by extrapolation of plots of E vs. $\log (1-x_t)$	0.06 - 0.13 mA ca. 0.2 to 0.5 V on polished electrode after pre-deposition	0.174 cm 0.154 cm
Initial potential on cathodic chronopotentiometry obtained oscillographically	0.03 - 0.4 mA 0.19 - 1.25 V	0.159 cm
Cathodic i - E curves in stirred solution	0 - 0.15 mA 0 - -.6 V	0.152 cm

(3) Effect of concentration in total absence of supporting electrolyte. Aqueous solutions of AgClO_4 were investigated over a wide range of concentrations. At each concentration chronopotentiograms were obtained at several currents to give transition times from 5 to 20 seconds. The value for d_L was obtained from the potential at $t = 0$ by visual extrapolation of the chronopotentiograms. The slope of E_M versus $\log (1-x_t)$ was plotted to give the sum, $k_C + k_D$. The results are shown in Table 7 below.

TABLE 7
Concentration Dependence of Electrochemical Measurements

Concentration of AgClO_4	$\frac{iT^{1/2}}{C}$	$k_C + k_D$	d_L
$\text{M} \cdot \text{l}^{-1}$	$\frac{\text{mA cm sec}^{1/2}}{\text{mM}^{-1}}$	V	cm
0.0001	630	.12	0.153
0.000295	620	.11	0.152
0.000583	610	.11	0.157
0.00113	620	.11	0.154
0.0049	620	.11	0.168
0.00962	630	.11	0.165
0.0293	630	.11	0.170
0.1	640	.12	0.170

At low concentrations the transition time is rather ill-defined. The initial potential plateau is followed by a slow linear increase in potential with time. To determine the transition time an extrapolation of this linear portion was drawn and the point at which the observed E-t curve just enters upon this linear portion was taken as the transition time. The slope of the linear portion was about $400 \times 10^{-6} \text{ C V}^{-1}$, corresponding to a capacitance of 400 uf. Surface effects were evidently small, for example, in the 0.0001 M solution the total current required to reach the transition time was only about 0.02 mC cm^{-2} whereas a monoatomic film is of the order of 0.2 mC cm^{-2} . The rather large values of d_L obtained in the higher concentrations was discussed in the preceding section.

(4) Effect of small additions of Supporting electrolyte. To an aqueous solution, 0.021 M in AgClO_4 , were added successive increments of LiClO_4 . Ideally the variation in $iT^{1/2}$ with supporting electrolyte is given by:

$$\frac{iT^{1/2}}{C} = \pi \frac{1/2 n F D_{\text{eff}}^{1/2}}{2} \frac{1}{1 - t_{\text{Ag}} +}$$

$D_{\text{eff}} =$ some effective diffusion coefficient which should be independent of concentration if ions migrate independently.

t_{Ag^+} = the transport number of the silver ion.

It is observed that in the absence of supporting electrolyte, when the transport number is about 0.5, $iT^{1/2}$ should be about double its value in the presence of excess supporting electrolyte, when the transport number approaches zero.

In the results shown in Table 8 below the transport number was calculated from the literature values for the equivalent ionic conductances of Ag^+ , ClO_4^- , and Li^+ (respectively: 62.5, 68, and 38.7 $\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$) and their concentrations.

TABLE 8
Effect of Transport Number on $iT^{1/2}$

Concentration of LiClO_4 M l^{-1}	$\frac{1}{1 - t_{\text{Ag}^+}}$	$\frac{iT^{1/2}}{C_{\text{Ag}^+}}$
0.000	1.925	630
0.005	1.67	550
0.010	1.52	502
0.0175	1.39	469
0.040	1.22	418
0.090	1.11	384
1.09	1.00	369

The slope of $iT^{1/2}/C$ versus $1/1-t_{\text{Ag}^+}$ is quite linear, being about $300 \text{ C M}^{-1} \text{cm sec}^{-1/2}$. The value for the expected slope based on an effective diffusion coefficient of $1.67 \times 10^{-5} \text{ cm}^2 \text{sec}^{-1}$ (calculated from the equivalent conductance from the Nernst equation: $D = \lambda RT/nF^2$) is $350 \text{ C M}^{-1} \text{cm sec}^{-1/2}$.

(5) Electrochemical measurements in other aqueous systems in the total absence of supporting electrolyte. A number of other aqueous systems

were examined to establish the general validity of the results obtained in the silver salt systems. We were concerned in measuring the effective d_L by a variety of methods and of determining mass transport parameters in terms of $iT^{1/2}$. The purpose of this is clear since, if general relationships can be established, the screening of unknown systems with respect to their electrochemical properties is greatly facilitated. In Table 9 below we show the effective d_L and the method by which obtained. We have not made any corrections for concentration polarization as discussed in the preceding section. In the limit of infinite dilution it can be shown that the following equation should be obeyed for the relationship between $iT^{1/2}$ and the limiting equivalent ionic conductance:

$$\frac{iT^{1/2}}{n_1 C} = \frac{\pi^{1/2} R^{1/2} T^{1/2}}{2} \cdot \left\{ \frac{(n_1 + n_2)}{(n_1 n_2) (1 - t_1)} \right\}^{1/2} \quad (6)$$

n_1 = the charge of the electroactive ion

n_2 = the charge of the counter ion

t_1 = the transport number of the electroactive ion

Using the literature values for equivalent conductance, and calculating the transport number from the equivalent conductances, the term in brackets has been computed. In Table 9 we show the quotient of $iT^{1/2}/n_1 C$ divided by this calculated term. This quotient should equal $\pi^{1/2} R^{1/2} T^{1/2}/2$, which is 44 at room temperature. The underlined ion in Table 9 is that for which $iT^{1/2}$ was found:

TABLE 9
Electrochemical Measurements in the Absence of Supporting Electrolyte

Salt	Concentration <u>M l⁻¹</u>	<u>d_L</u> <u>cm</u>	Quotient
<u>AgClO₄</u>	0.0021	0.157 (E-t at t = 0 by CRO)	40
<u>AgNO₃</u>	0.002	0.159 (E-t at t = 0 by CRO)	43
<u>Pb(NO₃)₂</u>	0.002	0.156 (E-t at t = 0 by CRO)	45
<u>Cu(NO₃)₂</u>	0.002	0.169 (Anodic E-t at t = 0)	43
<u>CuSO₄</u>	0.0018	0.144 (Cathodic E-t at t = 0)	47
<u>CuCl₂</u>	0.002	0.163 (Anodic E-t at t = 0)	39
<u>CuCl₂</u>	0.002	"	48
<u>KI</u>	0.002	0.156 (Anodic i-E on Ag ⁰)	43
<u>HCl</u>	0.001	--	42
<u>HCl</u>	0.001	--	42
NH ₄ Cl	0.001	0.155 (Anodic E-t on Ag ⁰ at t = 0)	--
K ₂ SO ₄	0.002	0.161 (Cathodic E-t at t=0 by CRO)	--
KOH	0.002	0.161 (Cathodic and anodic E-t at t = 0 by CRO)	--
K ₂ CP ₂ O ₇	0.003	0.166 (Cathodic E-t at t=0 by CRO)	--

The results are, in general, remarkably good. It is clear that meaningful electrochemical measurements may be made in the total absence of supporting electrolyte and information concerning electrokinetic limitations and the nature of the migrating species deduced therefrom.

b. Electrochemical measurements in non-aqueous solution in the total absence of supporting electrolyte.

(1) Reduction of AgClO_4 in propylene carbonate. A propylene carbonate solution, 0.02 M in AgClO_4 , was examined. Satisfactory chronopotentiograms were obtained on polished silver electrodes for the reduction of the silver ion yielding a value for $iT^{1/2}$ of $1.05 \text{ mA sec}^{1/2}$ on the 0.196 cm^2 electrodes. (Compare with the value of $2.60 \text{ mA sec}^{1/2}$ in 0.02 M aqueous AgClO_4 , indicating an effective diffusion coefficient in propylene carbonate of only about one-fifth that in aqueous solution). The effective d_L was measured from the specific resistance (1910 ohm-cm) and the potential observed by visual extrapolation to $t = 0$ from the $E-t$ curves, and was $0.150\text{--}0.151 \text{ cm}$. in satisfactory agreement with the values obtained in aqueous solution. The effects of varying transport number were observed by adding increments of LiClO_4 . The results are shown in Table 10 below. The transport number was calculated simply by assuming the ionic conductances of silver, lithium, and perchlorate ions to be equal.

TABLE 10
Reduction of AgClO_4 in Propylene Carbonate Following Addition of LiClO_4

Concentration of LiClO_4 M l^{-1}	Transport Number	$\frac{iT^{1/2}}{C}$ $\text{mA sec}^{1/2} \text{ cm}^2 \text{ mM}^{-1}$	E_M vs. $\log (1-x_t)$ V
0	.5	263	0.20
0.02	.25	200	0.09
0.04	.17	187	0.08
0.10	.08	179	0.06
0.2	.05	163	0.06

As expected, the value of E_M vs. $\log(1-x_L)$ decreases with increasing supporting electrolyte since k_D in equations 2-5 decreases. It is noted that the value in the unsupported solution is markedly higher than the expected value of 0.12 V -- that obtained in aqueous solution.

(2) Electrochemical behavior in propylene carbonate solutions of LiClO_4 . Satisfactory steady state E-i curves cannot be obtained in propylene carbonate solutions of LiClO_4 . At constant current the potential increases with time; at constant potential the current decreases with time. Nevertheless the following facts are observed:

(a) At potentials positive to the lithium deposition potential background reduction does occur. Initially high currents rapidly decay to less than 0.05 mA cm^{-2} within a few seconds. Prolonged reduction produces a tarry film on the electrode which is not removed by aqueous mineral acids or by any common organic solvents. The amount of background reduction at these potentials is markedly enhanced when observed on active silver electrodes of large surface area or when concurrent with the reduction of silver ions in solution. We believe this reduction to be that of solvent, the tarry product of which deactivates the surface and increases the overvoltage for subsequent reduction to potentials more negative than the lithium deposition potential.

(b) When E-i curves for lithium reduction are corrected for iR drop (using an effective d_L of 0.157 cm) it is observed that the efficiency for lithium deposition is constant up to about -0.2 to -0.3 V. versus a lithium electrode in the same solution. The average steady state current increases with increasing potential yet the efficiencies remain about 80% regardless of the current. We believe that, in this potential region, lithium reduction occurs presenting fresh active surface for the reduction of solvent. It may be expected that the rate of solvent reduction is proportional to the rate at which fresh surface is formed, in which case the fraction of current consumed by solvent reduction would be constant.

(c) At potentials more negative than about -0.3 V versus the lithium deposition potential, limiting currents are obtained. However, the amount of current consumed through the formation of metallic lithium steadily decreases. At -1.5 V the current is the same as at -0.5 V (corrected potentials) yet the efficiency of lithium deposition at -1.5 V is negligible. A black film of Li_2O or LiOH forms at these more negative potentials. These results clearly indicate that at these more negative potentials a reduction process occurs which consumes lithium ions not through the formation of lithium metal but through the formation of O^{--} or OH^- and subsequent precipitation of Li_2O or LiOH at the electrode surface.

(3) Electrochemical behavior of other solutes in propylene carbonate.

Solutions of LiCl , CsF , KI , and KCNS in propylene carbonate were examined. The potassium salt solutions were made 0.01 M; the solutions of LiCl and CsF were prepared by allowing an excess of salt to be stirred with the solvent for several hours. The results are discussed below:

(a) LiCl solution: The specific resistance of the solution was about 5000 ohm-cm, the same as that of the 0.01 M KI and KCNS solutions from which we estimate the concentration of LiCl to be about 0.01 M. A one-electron process in a solution of this concentration should yield an $i\text{T}^{1/2}$ of about $.4$ mA sec $^{1/2}$ on a 0.196 cm 2 electrode. On cathodization on silver or platinum reduction occurred at about -1.5 V versus a silver disc reference electrode (corrected for $i\text{R}$ drop) and an ill-defined transition time yielding an $i\text{T}^{1/2}$ of $.3$ to $.4$ was observed. Thereafter the potential rose to about -3.1 V and some lithium deposition was evident; however, efficiencies were low. Attempts to form anodic deposits of silver chloride were unsuccessful, the results indicating the anodic product to be soluble.

(b) CsF solution: Solutions of this salt were examined in the hope that sufficient solubility would occur to enable one to study the behavior

of the silver and copper electrodes in fluoride media. No evidence for the deposition of cesium metal was obtained on cathodization and background reduction occurred at -0.4 V. The anodization of copper resulted in the formation of a passivating film which could be reduced with 75 to 100% efficiency. The over-voltage for the oxidation of copper was extremely large and this process is not useful. The anodization of silver produced a reasonably insoluble salt which could be reduced with 75 to 90% efficiency; however, the CsF is not sufficiently soluble to form a useful electrolyte. The specific conductance was about half that of the 0.01 M KO and KCNS solutions indicating a solubility of CsF of only about 0.005 M.

(c) KI solution: Results on cathodization were similar to those obtained in the LiCl solution. Background reduction occurred at -1.2 V with an $iT^{1/2}$ of 0.26 to 0.3. No deposition of potassium metal was observed.

(d) KCNS solution: Results on cathodization were similar to those obtained in the LiCl and KI solutions. Background reduction occurred at about -2.3 V with an $iT^{1/2}$ of about 0.45. No evidence of potassium metal deposition was observed. Anodization of silver and copper electrodes in this solution did not evidence the formation of insoluble films.

It is interesting to observe that the amount of cathodic background reduction is about that expected for one-electron reductions in solutions of 0.01 M. This suggests that the cations are intimately involved in the cathodic decomposition reactions. The examination of dilute solutions may be the desirable method for the determination of solvent impurities or of studying the solvent decomposition itself.

III. Practical Cell Studies

A. Porous Electrodes

In previous studies measurement of transition time due to concentration polarization has been established as a convenient criterion for studying the behavior of flat electrodes. Based on the results obtained it has been possible to discuss the performance of the Li/LiCl , AlCl_3 system, in propylene carbonate solution. In utilizing this information for high energy density electrodes in practical cells, it is obvious that one has to look for maximizing the utilization of active materials by employing conventional porous electrodes, or other new types of electrode configurations. The particular utility of porous electrodes or any new configuration has to be evaluated by systematic studies of the additional problems that arise in maximizing. For example, considering the conventional porous electrodes, its performance differs from that of flat electrodes due to complex double layer charging, IR drop inside the pores, concentration polarization, etc. These parameters not only depend on physical characteristics such as pore size, per cent porosity, and thickness of the plate, but also on experimental conditions such as conductivity of solution, current density, and configuration of assembly. The various interlinked parameters affecting the behavior of a given electrode is complex and cannot be anticipated. This has to be evaluated by carrying out actual experiments, preferably in relatively simple systems so as to allow for deriving conclusions for systems of our interest, viz. high energy density electrodes.

The purpose of the work done during the reporting period is to establish suitable criteria for evaluating the relative performance porous electrodes. In order to accomplish this, the copper/copper sulfate system in aqueous solution was chosen for study and from the preliminary experiments carried out, it has been possible to conclude, that the chronopotentiometric technique is suitable for the purpose. This conclusion was arrived at by comparing the behavior of flat electrodes with typical porous electrodes.

Cathodic chronopotentiometric measurements involving deposition of copper onto inert flat and porous electrodes were carried out in an acidified aqueous solution of 0.01 N Cu SO₄ in N Na₂ SO₄. A copper electrode in the working solution served as reference electrode for recording potential-time curves. Both types of electrodes display transition point due to concentration polarization. The data on the transition time measurements at different current densities is given in the following two tables:

TABLE 11

Chronopotentiometric Behavior of Flat Electrodes

Current i, mA	Transition Time T, sec.	$iT^{1/2}$ mA sec ^{1/2}	Remarks
1.5	60	11.6	Since the experiments are directed towards the study of nature of behavior rather than studies on particular species, the emphasis has been on overall reproducibility, not on accuracy of measurement. Hence, a deviation of $\pm 15\%$ from the mean has been allowed in drawing conclusions.
2	29.2	10.84	
2.5	18.3	10.7	
3.75	8.06	10.65	
5	6	10.61	
6.25	4.25	11.5	
7.5	1.9	10.4	
10	1.04	10.2	
12.5	0.66	10.2	
15	0.44	9.95	
17.5	0.3	9.65	
20	0.21	9.15	
25	0.12	8.65	
35	0.064	8.85	
50	0.03	8.7	
65	0.016	8.25	
75	0.011	7.85	
85	0.009	8.05	
100	0.0064	8.00	

The values of $iT^{1/2}$ for the flat electrodes is fairly constant and this is in accordance with semi-infinite normal diffusion to flat surface. The data when plotted as iT against $1/i$ gives a straight line. (Fig. 1, Curve A)

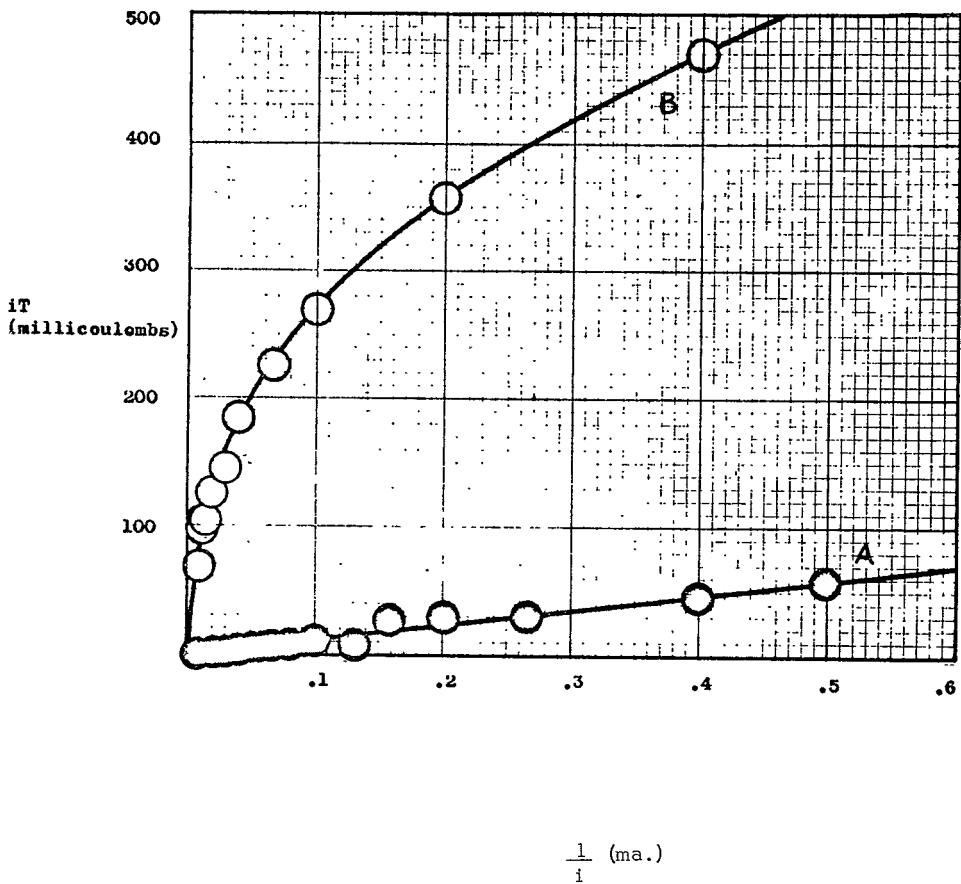


Figure 1: COMPARISON OF CHRONOPOTENTIOMETRIC BEHAVIOR ON FLAT AND POROUS ELECTRODES.

Curve A -- flat copper electrode

Curve B -- Porous steel electrode

TABLE 12

Chronopotentiometric Behavior of Porous Electrode*

Current i, mA	Transition Time T, sec.	$iT^{1/2}$ mA. sec ^{1/2}	Remarks
2.5	187.8	34.2	Same as for Table 11
5	71.3	42.3	
10	27	52.0	
15	15	58.1	
25	7.41	68.3	
35	4.13	71.0	
50	2.5	79.0	
65	1.6	82.2	
75	1.4	88.9	
85	1.16	91.8	
100	0.68	82.6	

* A cylindrical stainless steel porous electrode of 1 cm diameter, 0.2 cm thick, 20% porosity was used with only one side of the flat face exposed to solution.

Curve (B) in Fig. 1 is obtained on plotting the data in Table 12 for the porous electrode in the form of iT against $1/i$. The type of plot is derived by squaring the Sand equation

$$T^{1/2} = \frac{\pi^{1/2} D^{1/2} n F A c^0}{2i}$$

where i is the current, A is the true electrode surface area in cm^2 , D is the diffusion coefficient in $\text{cm}^2 \text{sec}^{-1}$; n is the number of electrons involved in the reaction, F is the Faraday, and c is the concentration in m l^{-1} in A cm^{-2} .

Thus the curve obtained for the porous electrode reflects changes occurring in both surface area and concentration of electroactive species within the electrode.

The investigation reveals the following information:

- (i) $iT^{1/2}$ is not constant for the porous electrode, and it decreases with increasing current.
- (ii) iT is significantly larger for the porous electrode than for the flat electrode.

From this study it can be anticipated that the exact nature of curve (B) in Figure 1 would depend on the physical parameters of the porous electrodes or electrode configuration. The best porous electrode will be the one with the highest iT values, and a less steep fall in iT values with increasing current.

It is planned to take up this study after investigating the behavior of a given porous electrode structure in Li/LiClO_4 systems.

B. Cell Systems

1. The Lithium/Lithium Chloride-DMF/Copper Chloride Cell

a. Solvent Selection

The most widely studied and employed cell system to date is Li/LiCl , $\text{AlCl}_3/\text{metal chloride}$ in propylene carbonate. However, it has been observed that aluminum chloride presumably reacts with the solvent and generates background materials which contribute to reduction of the current efficiency of the lithium electrode. The literature available on studies made on employing other solvents seems to be inadequate for arriving at a conclusion regarding the compatibility of other solvents. From this point of view, it was felt necessary to investigate other solvents. In this reporting period, investigations have been carried out employing dimethylformamide (DMF) as solvent.

The basis for selection of DMF as a probably suitable solvent are the following:

- (1) Lithium chloride dissolves in DMF to give solutions that are as

conductive as lithium chloride-aluminum chloride solutions in propylene carbonate.

(2) Lithium chloride solutions in DMF are stable on standing, unlike lithium chloride-aluminum chloride in propylene carbonate.

(3) DMF has a lower density and viscosity than propylene carbonate.

(4) The melting and boiling points of DMF and propylene carbonate are similar.

Based on these considerations it was decided to carry out electrochemical measurements to test the general performance of cells using DMF as solvent.

b. Anode Selection

The electrodeposition of lithium was studied on two inert electrodes-copper and aluminum-in DMF solutions with the following results:

(1) Performance of Lithium on Copper Electrodes

Electrodepositions of lithium were carried out from 1M LiCl solutions in DMF employing copper as an inert electrode. It was observed that the current efficiency of the system was close to 40% using a copper chloride counter electrode. Pilot cells were constructed, as described later, to estimate the cell performance. Measurements of cell efficiency indicated that current efficiency was close to 20-30% when tested for 100 to 300 mC cm⁻² of charge. The open circuit voltage after deposition was 2.65 ± 0.05 volts. Polarization was about 300 mV for discharge at 2.5 mA cm⁻².

(2) Performance of Lithium on Aluminum Electrodes

From the point of view of reducing the dead weight of inert electrodes, aluminum was tried as an inert conductor for the lithium deposition. In this case it was observed that there was an increase in current efficiency over the copper electrode from 40 up to 80%. Employing a similar pilot cell as for copper, the

performance of the aluminum electrode was tested for cycling. The current efficiency remained the same on repeated cycling, suggesting that aluminum could be effectively used as an inert electrode material. The open circuit voltage on deposition was again 2.65 ± 0.05 volts.

The reason for the low efficiency of the copper electrodes in comparison to aluminum may be any of the following:

(i) The overpotential of reduction of solvent may be lower on copper than on aluminum.

(ii) It is conceivable that in the case of aluminum, the presence of a surface oxide layer may prevent surface alloying of lithium with aluminum and thus effect higher recoveries.

(iii) Because of a lower E.M.F. difference between lithium and aluminum than between lithium and copper, the possible corrosion currents between lithium and the inert electrode decrease. This would mean a more effective retention of active material on aluminum and this is the observed behavior.

(3) Confirmation of Lithium Electrode Reaction

The efficiency of the lithium electrode used in the practical cell studies was determined by a technique similar to that previously used for the multi-disc lollipop electrodes. An amount of lithium, measured by means of its electrochemical equivalent charge, is deposited on a clean copper electrode from a lithium chloride-DMF solution. The lithium deposit is then allowed to react completely with water to generate lithium hydroxide. The resulting alkali is then titrated with standard acid to determine the chemical equivalent present. The electrode is then charged again to the same number of coulombs and the lithium deposited estimated from anodic discharging.

(a) Chemical Estimation of Lithium Electrode Efficiency

In a typical experiment, a cathodic charge of 20,000 millicoulombs

was put on a 10 sq. cm. copper electrode at a current of 20 mA. By anodically discharging at 20 mA it was possible to recover 18,000 millicoulombs up to a cut-off voltage of 1.5 volts versus an Ag electrode in the same solution. The 20,000 millicoulomb deposition step was then repeated and the LiOH formed from the reaction of the electrodeposit with water was titrated with standard HCl using a pH meter. It required 1.63 ml of 0.118 N HCl, equivalent to 18,560 millicoulombs, to completely neutralize the LiOH. Thus it is seen that the current efficiency of lithium formation and recovery under these conditions is 90 to 95%.

(b) Lithium Electrode Potential Behavior

A study of the behavior of the non-aqueous lithium electrode with change in lithium ion concentration was carried out in order to verify that the Nernst relationship is obeyed by the Li/LiCl system.

An H-type of cell, consisting of two compartments separated by a fine glass frit, was used for the experiment. One limb of the cell was filled with 1 N LiCl in DMF, while the concentration of LiCl in the other compartment was varied. Lithium electrodes were immersed in each compartment and the potential difference between the two electrodes measured. The steady state potentials were established almost immediately and therefore it was possible to complete the potential measurements before any appreciable mixing of the two solutions took place. The results are given in Table 13.

TABLE 13

Variation in Potential of Li/LiCl Couple with
Concentration of Lithium Chloride

<u>System Used</u>	<u>Potential Volts</u>
Li/0.0001 N LiCl// 1N LiCl/Li	+ .230
Li/0.001 N LiCl// 1N LiCl/Li	.160
Li/0.01 N LiCl// 1N LiCl/Li	.115
Li/0.1 N LiCl// 1N LiCl/Li	.058
Li/1.0 N LiCl// 1N LiCl/Li	.002

A plot of the potential versus the logarithm of concentrations is linear, with a slope of about -0.06 V.

c. Cell Assembly

One square centimeter of aluminum foil (99.99% pure) was cut from a layer piece of foil leaving a strip of aluminum for the lead, and was packed in a fibre glass separator. Adjacent to the pack of aluminum electrode, a 70% porous copper electrode one of square centimeter area was placed and the assembly held in position by wrapping the same with glass fiber strings. The electrode assembly thus prepared was immersed into a 50 ml. glass wide mouth bottle containing 1M lithium chloride solution in DMF. The electrode leads were passed through slits cut in the plastic snap-on bottle caps and supported the assembly in the solution.

d. Cell Performance

The following experimental variables were then investigated using the cell assemblies just described.

- (1) Behavior under the same charge-discharge currents.
- (2) Behavior under constant current charge with variable discharge

currents.

(3) Behavior under variable charging currents with constant discharge current.

(4) Behavior under constant current charge with discharge through an external load.

(5) Behavior of the Cell on the extent of charging.

(6) Behavior of the charged cell on open circuit stand.

(7) Behavior of the cell on cycling.

Investigations from (1) to (3) were conducted employing current densities from 0.25 ma/cm^2 to 2.5 ma/cm^2 by charging the cell up to 300 mC total charge and discharging instantaneously after charge. The results, shown in Table 14 below, seem to indicate that in the current density range of study, the efficiency does not change with variations in either charge or discharge current. The observed efficiency is seen to be in the order of $70 \pm 10\%$.

TABLE 14

Efficiency of Lithium-Copper Chloride Cells During
Variations in Charge and Discharge Currents

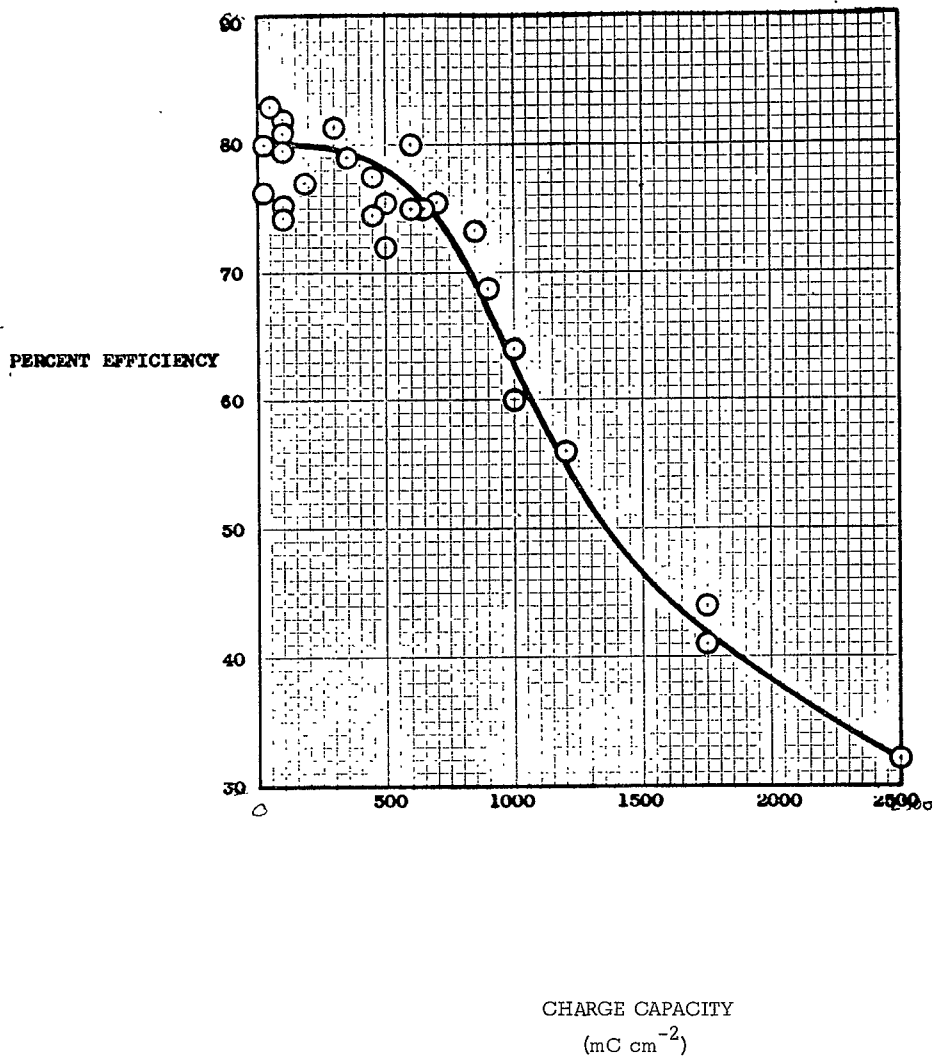
<u>Charging</u> <u>Current, ma.</u>	<u>Discharge</u> <u>Current, ma.</u>	<u>Efficiency</u> <u>%</u>
0.25	0.25 - 2.5	65 - 75
0.50	0.25 - 2.5	"
1.00	0.25 - 2.5	"
2.50	0.25 - 2.5	"
0.25 - 2.5	0.25	"
0.25 - 2.5	0.50	"
0.25 - 2.5	1.00	"
0.25 - 2.5	2.50	"

In order to investigate behavior of (4), the cells were discharged through an external resistance of 3000 ohms. A current of 1.0 to 1.5 ma. was obtained under these conditions. It was observed that the discharge characteristics of the cells were of the same nature as obtained by reversing the current from a constant current power supply. The cell efficiency during discharge was measured with a coulomb integrator. The discharge efficiency remained at the same value, $70 \pm 10\%$, throughout 40 cycles.

For experiment (5), the cell was charged to various amounts from 25 mC to 25000 mC at 1 ma/cm^2 and discharged at the same current density. The efficiency was measured at each different amount of charge and is plotted in Figure 2 as cell efficiency versus coulombs of charge. These results indicate that the cell could be operated with 75% efficiency, up to a total charge of 700 mC/cm^2 . On charging beyond this capacity, the efficiency decreases steadily and by nearly three times the critical charge of 700 mC/cm^2 it has dropped to around 35%. It should be recognized that these results include the superimposed effects of any self-discharge taking place.

In order to study the behavior of the charge retention of the cell on open circuit stand, (6), the cell was charged to 300 mC in each case and let stand for known intervals of time. The cell was then discharged and the efficiency of recovery determined. Figure 3 shows the results obtained. It can be seen that the cell undergoes almost complete charge loss in the course of 80 minutes. The probable causes of this behavior may be one or more of the following:

- (i) Solvent oxidizing the lithium electrode or dissolving copper chloride from the cathode.
- (ii) Dissolved copper chloride reacting with lithium electrode.
- (iii) Poor quality of the separator which allows colloidal copper chloride, if any is present, to migrate across to the lithium electrode.



The cell behavior on cycling, (7), can be ascertained from experiments (1) to (6) in which the cell has been subjected to close to 100 short cycles without any appreciable change in efficiency. Furthermore, the 40 cycles which the cell has undergone during discharge through an external load suggests that the cycle life of the cell is fairly good. Cycling was conducted at 1 mA cm^{-2} for 300 on C m^{-2} of total charge.

e. Self-Discharge Mechanism Study

In view of the results of experiment (6) in part d. above in which the cell under went complete charge loss in 80 minutes, investigations were carried out to systematically evaluate the probable causes of self-discharge. Since the self-discharge of the cell has been observed to occur in about $1 \frac{1}{2}$ hours, the preliminary investigations reported herein were directed towards understanding events transpiring in time intervals of a few hours. The following experiments were conducted in this regard.

(1) Lithium Electrode Efficiency After Open Circuit Stand

The first set of experiments consisted of determining the charge retention of lithium electrodes in 1 M LiCl in DMF. A quantity of lithium equivalent to 300 millicoulombs of charge was deposited on a one square centimeter aluminum electrode. The lithium electrode thus generated was allowed to stand on open circuit for 2 hours in 1 M LiCl in DMF. It was observed that there was no difference between the discharge efficiency of this electrode and that of electrodes discharged instantaneously after formation. It is therefore evident that there is no contribution from a depolarizing reaction of solvent with lithium electrodes to the short term self-discharge of the cell.

This experiment also excludes the possibility of any appreciable self-discharge due to impurities such as dissolved oxygen and moisture present in the solvent. However, this does not exclude the above factors from consideration with respect to long term self-discharge effects and studies regarding these

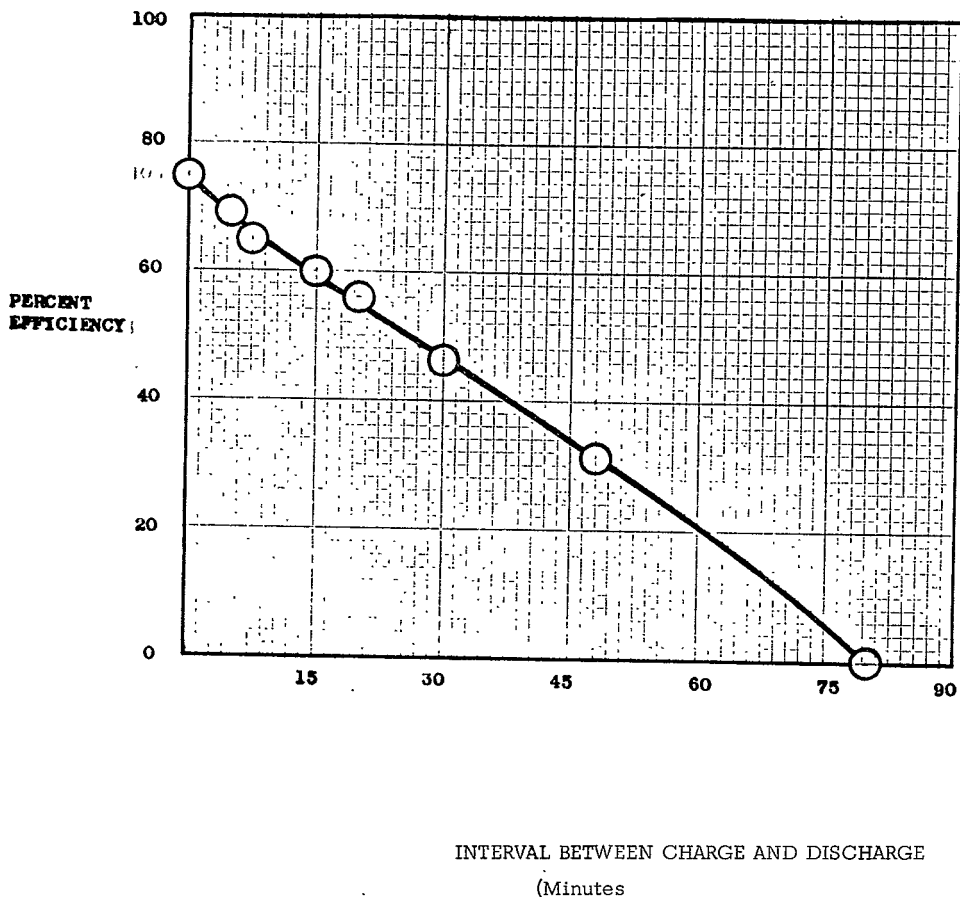


Figure 3: EFFECT OF LENGTH OF OPEN CIRCUIT STAND TIME AFTER CHARGING ON EFFICIENCY OF A LITHIUM-COPPER CHLORIDE CELL IN DIMETHYLFORM-AMIDE.

effects will have to be taken up as improved cells are fabricated.

(2) Examination of a Used Cell

(a) Lithium Electrode

Examination of a lithium electrode from a used cell revealed that copper had been deposited on the aluminum substrate, doubtless through reduction of soluble copper salts by the aluminum metal.

(b) Copper Electrode

The porous copper electrode from a used cell had a yellow film of copper halide and also some black film. The black film may be copper oxide, formed through discharge of dissolved moisture or oxygen, or electrochemically generated tar from decomposition of the solvent. Since the black material was not easily removed by dilute HCl, it is concluded that the substance is organic, probably the tar produced by solvent decomposition.

(c) Separator

The separator used in constructing the cell was fiber glass cloth. It was observed that the cloth became yellowed through impregnation by soluble copper salts.

(d) Electrolyte

The originally clear colorless 1 M LiCl solution was found to turn yellow after use in the cell. The total concentration of yellow material was estimated chronopotentiometrically to be in the range of 0.1 to 0.01 grams per liter. The yellow color observed is presumably connected with the solubility of copper salt. In order to identify the copper species present in the solution, the spectra of the electrolyte used in the cell was plotted with a Bausch & Lomb Spectronic 20 and compared with that of CuCl in DMF and CuCl_2 in DMF. Figure 4 gives the spectra of the three samples in the visible region. Comparing

the absorption at 3700 \AA it can be seen that the electrochemically generated yellow substance consists of both cuprous and cupric salt. A more detailed quantitative interpretation depends on further work in establishing Beer's law for the system of interest and in determining the limiting solubility of cuprous and cupric salts.

From the above experiment it can be concluded that the copper electrode reaction involves a mixed potential of various Cu (I) and Cu (II) species. Since the equilibrium potentials and exchange currents of the single electrode system of Cu (I) and Cu (II) have a large influence of the overall cell potential, open circuit potential measurements of Cu/Cu (I) and Cu/Cu (II) were conducted. Table 15 gives the data from these measurements. It is seen that as in aqueous systems, the potentials of Cu (I) chloride and Cu (II) chloride are close to each other and cannot be easily distinguished after subjecting the electrodes to charge-discharge cycling. Until further fundamental studies are carried out to evaluate the electrode kinetic parameters, it is reasonable to assume at this stage that the potentials observed are mixed potentials.

(3) Copper Chloride Solubility Determination

In dealing with the self-discharge problem as relates to the solubility of cathode salts, it is of interest to examine solubility limits that could be set in selecting the cathode salts. No generalization is possible in this regard as the solubility limits depend on the purpose for which the cell or battery is designed to be used. For example, in case of short life reserve cells, the problem of self-discharge after activation is of minor importance; while for energy storage cells, it is necessary to keep the self-discharge rate as low as possible. Assuming that all the self-discharge of present day aqueous battery systems is due to dissolved cathode material, the working limits of solubility for cathode material in a comparable non-aqueous cell could be fixed as at least lower than $5 \times 10^{-4} \text{ m l}^{-1}$. This is about the solubility of AgO , HgO , CdO ,

TABLE 15

Open Circuit Potentials of Copper/Copper Salt Couples
in 1 M LiCl-DMF Solution

<u>Cu/Cu Salt Couple</u>	<u>Pasted Electrode Potential, Volts</u>	<u>OCV After Charge, Volts</u>	<u>OCV After Discharge, Volts</u>
Cu/CuCl [*]	-0.180	-0.180	-0.24
Cu/CuCl ₂ [*]	-0.23	-0.20	-0.24
Cu/CuO ^{**}	+0.05	not measured	not measured
Fresh copper electrode in 1 M LiCl ^{***}	-0.210	-0.12	-0.21

Notes:

All measurements versus Ag electrode in same solution (± 0.03 mv.)

* Copper salt paste in DMF is applied on a clean copper foil.

** Copper oxide formed by heating Cu in air.

*** Copper foil cleaned in HCl, rinsed with distilled water, and dried with acetone.

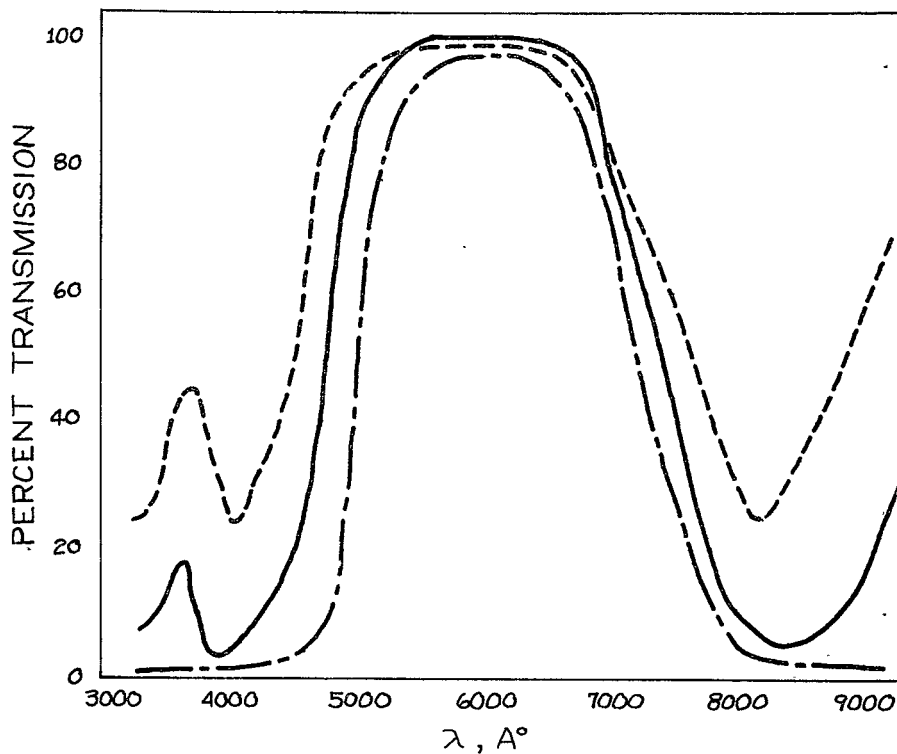


Figure 4:

COMPARISON OF VISIBLE SPECTRA OF USED CELL ELECTROLYTE,
COPPER (I) CHLORIDE, AND COPPER (II) CHLORIDE.

- — — Used Cell Electrolyte
- — — CuCl in DMF
- CuCl₂ in DMF

etc., in aqueous KOH as battery electrolyte.

With this figure in mind the solubilities of CuCl and CuCl_2 were determined gravimetrically in DMF at room temperature. Saturated solutions of each were prepared and aliquot portions were carefully evaporated to dryness and the residues weighed, checked on terms of residue. Solubilities thus obtained were 0.05 m l^{-1} for CuCl and 2.5 m l^{-1} for CuCl_2 . The order of solubility observed is too high for consideration as cathode salts and the self-discharge of the cell could be completely accounted for.

f. Attempts to Decrease Copper Chloride Solubility in DMF

In order that the Li/LiCl-DMF/CuCl , CuCl_2 system might be further considered for utilization in a high energy density battery, the following attempts were made to reduce the solubility of the copper salts in DMF.

(a) Effects of Common Ion Variations

Solutions of LiCl in DMF in which the LiCl concentration was changed from 0.1 M to saturation (3M) were used to study the effect of chloride ion concentration on copper chloride solubility as measured by the self-discharge rates of experimental cells. It was observed that altering the LiCl concentration did not reduce the copper chloride solubility to within the required limit (i.e., $< 5 \times 10^{-4} \text{ M/L}$).

(b) Effects of Mixed Solvents

It would be anticipated that, if to a solution of copper salt in DMF, another solvent which is miscible in DMF, but is a non-solvent for copper salt, be added, then the copper salt solubility would be decreased. In dealing with the method of insolubilization it should be realized that there are other requirements such as that the added solvent should be stable in the presence of deposited lithium, and should not alter the conductivity of LiCl solution appreciably, etc. A search was made to select a suitable solvent for the purpose. A typical solvent employed for the purpose was toluene. In a 3:2

mixture of DMF and toluene, LiCl was soluble to the extent of 1 m l^{-1} , and the solution conductivity had only changed from $7 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ to $4 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ due to addition to toluene. However, it was observed that copper salt solubility was greater than 0.5 g/100 ml. of 1M LiCl solution, indicating the method was ineffective. Similar results were observed while employing either propylene carbonate or tetrahydrofuran as co-solvents in DMF, and hence the method had to be given up.

(c) Effects of Complexing Anions

Attempts were made to change the solubility of copper salt through complex formation with other added anions. Table 16 gives the complex forming anions employed. To a solution of 1M LiCl containing 1% CuCl_2 in DMF, excess complex forming salts were added, and precipitation was looked for as a criterion of insolubilization.

TABLE 16

Effect of Complexing Anions on the Solubility of Cathode Salt

<u>Added Salt</u>	<u>Expected Complex Salt</u>	<u>Result</u>
KCNS	$\text{Cu}(\text{CNS})_2$ etc.	Blood Red Solution
KI	CuI_2 etc.	Brownish Red Solution
KPF_6	$\text{Cu}(\text{PF}_6)_2$ etc.	Yellow Solution

g. Conclusions

The general characteristics of the Li/LiCl-DMF/ CuCl/Cu couple are very encouraging from the point of view of charge-discharge behavior and cycle life. However, the severe short term self-discharge characteristics, which can only be overcome by finding a means to reduce the solubility of the

copper chloride salts, present a serious problem that limits the utility of the system.

2. The Lithium/Lithium Tetrafluoroborate- γ -Butyrolactone/Copper Salt Cell

While investigating alternative systems to $\text{Li/CiCl-DMF/CuCl}_x/\text{Cu}$, the general concept of increasing the solubility of lithium salts by means of complex formation with Lewis acids was pursued. As a result it was found that the normally very insoluble lithium fluoride would dissolve in organic solvents which contained boron trifluoride etherate. The formation of lithium tetrafluoroborate was indicated by the fact that ether was liberated and could be removed by vacuum distillation under nitrogen gas. The heating also causes some decomposition of solvent to give brown solutions similar to those encountered with aluminum chloride. By using this technique lithium fluoride was dissolved in propylene carbonate, dimethylformamide, γ -butyrolactone, acetonitrile, and tetrahydrofuran. A 1M butyrolactone solution prepared in this way had a specific conductivity of $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ and it was found possible to deposit lithium from it. However, due to the large background currents encountered ($> 5 \text{ ma/cm}^2$), it is felt that the preparative method must be improved and standardized before an experimental cell can be constructed and evaluated.

IV. Future Work

During the first month of the next quarter studies similar to those outlined in this report will be completed in order that the maximum amount of information be realized from the electrochemical data obtained in the subsequent screening program.

The following screening program will then be undertaken:

(a) The lithium-copper halide system has demonstrated merit. The preliminary objective of the initial screening will be to find those electrolytes in which the copper electrode may be most efficiently cycled.

(1) The solubility of CuF_2 , Cu_2Cl_2 , and CuCl_2 will be determined in the following solvents, in each case using each of the four lithium salts indicated:

Solvents:

Butyrolactone
Tetrahydrofuran
Propylene Carbonate
Dimethylformamide

Salts:

LiClO_4
 LiBF_4
 LiAlCl_4
 LiCl

Salt will be added to solvent for each of the sixteen combinations in the amount required to yield a 0.1 M solution if completely soluble. To each of the sixteen solutions will be added an amount of the appropriate copper salt yielding a 0.05 M solution if completely soluble. The solutions will be allowed to equilibrate for one week. Each of the forty-eight systems will then be investi-

gated polarographically, by which satisfactory estimates of the concentration of dissolved copper can be made to within 30% from the limiting current.

(2) Those systems in which the solubility of copper is less than 10^{-3} M will be further investigated on flat copper electrodes. Anodic-cathodic cycling will be performed at from 0.1 to 10 mA cm⁻² to determine the degree to which insoluble products are produced on anodization. Those systems exhibiting some degree of formation of insoluble anodization products will be subjected to prolonged anodization of massive copper electrodes and the nature of the products determined.

(3) Those systems in which the solubility of copper is less than 10^{-3} M will be further examined using compacted copper halide electrodes. These will be prepared by compacting a mixture of the halide and powdered copper metal into the lollipop disc electrode system. Such electrodes will be prepared to receive the compacted mixture by partial electrolytic etching of the copper disc, providing a recess into which the cathodic mixture may be pressed. The efficiency of cathodic-anodic cycling will be determined up to 25% depth of discharge, at from 1 - 50 mA cm⁻².

(4) Results: The two best solvent-lithium salt-copper salt systems will be selected and developmental work commenced on prototype electrode fabrication.

(b) The lithium electrode will be further examined for those systems in which the solubility of copper halide is less than 10^{-3} M. Preliminary screening will be obtained from a proper analysis of the electrochemical measurements obtained in the first section. Special attention will be given to the polarographic measurements which give some indication of the impurity levels and the solvent decomposition potential (on mercury).

(1) Those systems in which the potential for lithium deposition precedes the decomposition of solvent by a discernible amount will be further examined on solid electrodes. The charge-discharge efficiency will be deter-

mined in the range of concentration from 0.1 M to saturation and from currents of 0.05 to 20 mA cm⁻².

(2) Particular attention will be given to the effects of pre-electrolysis and the presence of dissolved oxygen and water. Each system will be routinely subjected to pre-electrolysis and the charge-discharge efficiency re-determined.

(3) Those systems having charge-discharge efficiency of better than 50% will be further examined in two ways. Massive lithium metal compacted into the recesses of the electrolytically etched lollipop disc electrodes will be discharged to a maximum of 25% depth at currents up to 20 mA cm⁻² to determine whether any limiting processes occur in the discharge of lithium metal. Lithium salts will be compacted into the recesses of the etched disc electrodes and cycled to determine whether discharge from the salt is markedly different from discharge from the solvated ion.

(4) Results: Those systems judged to have merit with respect to the efficiency of cycling and to the ability of the electrolyte to sustain satisfactory copper halide electrode behavior will be selected for development into prototype battery electrodes and the cycling behavior further examined.

(c) A concurrent screening program will be concerned with the examination of potentially electroactive materials which cannot be examined on flat, polished metal electrodes.

(1) Mixtures of CoF₃, MaF₃, and CrF₃ will be compacted into the recesses of the etched disc electrodes. Initially screening will be only concerned with the degree to which any reversible cycling is obtained. Initial experiments will be conducted in propylene carbonate solutions of LiClO₄, but the results of the above screening program will indicate more useful electrolytes.

(2) Oxide electrodes are not unfeasible if an electrolyte can be found in which the alkali salt oxide or hydroxide produced on discharge is

sufficiently insoluble to remain at the cathode surface and yet does not passivate the electrode during discharge. As yet sufficient information does not exist concerning potentially applicable electrolytes. Consideration will be given, however, to the discharge of compacted discs of Ag_2O , AgO , Cu_2O , MnO_2 , and NiO(OH) .

(3) Satisfactorily efficient cycling has, to date, been obtained from solution only for the lithium electrode. Investigation of the cycling behavior of compacted discs of calcium, magnesium, and sodium salts will be considered.

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